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# Laser Raman and infrared spectra of some uracil derivatives*

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The N-heterocyclic molecules e.g. pyrimidine, cytosine, uracil and their derivatives are of considerable biological and pharmaceutical importance (Handschumacher and Welch 1960, Martin 1961). Recent spectroscopic studies of these compounds have been motivated because the vibrational spectra of free base molecules is very useful for the understanding of specific biological processes and in the analysis of relatively complex systems. Along the macromolecular double-helix chain, the vibrational modes of each base interact with those of other bases through hydrogen bonds or stacking effects and these interactions affect the ring vibrations. The vibrational spectra of various nucleic acid constituents including uracil have been studied in detail (Angel 1961, Lord and Thomas 1967, Susi and Ard 1971, Susi *et al* 1973, Bandekar and Zundel 1983, Singh *et al* 1987), but very little work on the vibrational spectra of derivatives of uracil has been done (Shimanouchi *et al* 1964, Sanyal *et al* 1977, Ferro *et al* 1980, Goel *et al* 1981, Aruna and Shanmugam 1985, Yadav *et al* 1988). In order to extend this study further, we have recorded the IR and laser Raman spectra of 5-chloro and 5-amino uracils for the first time and assigned the observed fundamental bands.

Pure solid samples of 5-chlorouracil (mp > 300 °C) and 5-aminouracil (mp > 300 °C) were obtained from M/S Sigma Chemical Co, USA and used as such without further purification. The IR absorption spectra have been recorded on Beckman IR-12 spectrophotometer in KBr pellet in the region 400-4000 $cm^{-1}$. The laser Raman spectra in the region 50-2000 $cm^{-1}$ (Raman spectra beyond 2000 $cm^{-1}$ are not worth-mentioning) have been recorded on a Spex spectrophotometer using Argon laser source with exciting radiations 5145 Å.

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Figures 1-3 show the structures of the uracil and 5-chloro and 5-amino uracils molecules with classical numbering of the atoms respectively. The vibrational spectra (IR and Raman) have been interpreted assuming planar geometry and $C_s$ point group symmetry for both the molecules and the observed fundamentals have been assigned to different normal modes of vibration. The vibrational modes are classified as transforming like the basis functions of the $a'$ and $a''$ irreducible representations. Thus the 30 fundamental modes of 5-chlorouracil may be classified into $21a'$ symmetry species (in-plane) and $9a''$ species (out-of-plane) and in

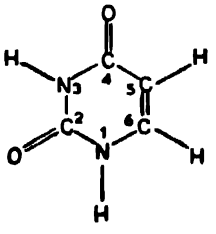

**Figure 1.** Uracil.

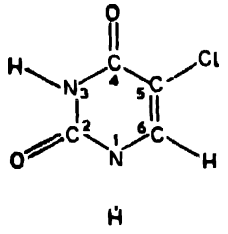

**Figure 2.** 5-Chlorouracil.

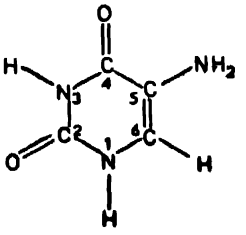

**Figure 3.** 5-Aminouracil.

the case of 5-aminouracil, the 36 fundamental modes may be classified into $25a'$ and $11a''$ symmetry species. The analysis of the bands and the assignment of the fundamental frequencies are made on the basis of magnitude and relative intensities of the observed bands and help has been taken from the assignments made by earlier workers in the similar molecules. The wavenumbers of the observed fundamental bands in IR and Raman spectra alongwith the proposed assignments are given in Table 1.

The frequencies due to CH/NH stretching modes are well separated from the frequencies due to other modes. The molecules under study contain only one hydrogen atom attached to the carbon atom of the ring (Figures 2 and 3) and thus involve only one C – H valence oscillation which have been identified at 3032 and 3018 $cm^{-1}$ in the IR spectra of the 5-chloro and 5-amino uracils respectively. These assignments are in agreement with those proposed by Ferro *et al* (1980) and Aruna and Shanmugam (1985) in the case of related molecules. The bands observed at 1422 $cm^{-1}$ (IR) and 1410 $cm^{-1}$ (Raman) in the case of 5-chlorouracil and at 1425 $cm^{-1}$ in 5-aminouracil have been assigned to C – H in-plane bending mode.

The N – H stretching was assigned by Susi and Ard (1971) at 3145 $cm^{-1}$ in 1-methyl uracil and at 3146 $cm^{-1}$ in 1-methyl thymine and by Sanyal *et al* (1977) at 3178, 3098 $cm^{-1}$ in 5-bromouracil, at 3188, 3128 $cm^{-1}$ in 5-methyl uracil and at 3178, 3107 $cm^{-1}$ in 4(6)-aminouracil. In the present case only one of the two N – H stretching modes could be observed at 3059 and 3080 $cm^{-1}$ in the IR spectra of 5-chloro and 5-amino uracils respectively.

The $NH_2$ group has two (N–H) stretching frequencies, one being symmetric and other asymmetric. The frequency of asymmetric vibration is higher than that of

**Table I.** Assignment of fundemental frequencies (in $cm^{-1}$) of 5-chloro and 5-amino uracils.

| 5-Chloro-uracil | | 5-Amino-uracil | | Symmetry species | Assignment |
|---|---|---|---|---|---|
| IR | Raman | IR | Raman | | |
| — | — | 3370 | — | a′ | $NH_2$ asymmetric stretch |
| — | — | 3295 | — | a′ | $NH_2$ symmetric stretch |
| 3059 | — | 3080 | — | a′ | N–H stretch |
| 3032 | — | 3018 | — | a′ | C–H stretch |
| 1705 | — | 1740 | — | a′ | C=O stretch |
| 1677 | 1676 | 1672 | — | a′ | C=O stretch |
| 1632 | 1625 | 1615 | 1645 | a′ | C=C stretch |
| — | — | 1588 | — | a′ | $NH_2$ scissor |
| 1560 | — | 1556 | — | a′ | N–H in-plane bending |
| 1542 | — | 1541 | — | a′ | N–H in-plane bending |
| 1509 | — | 1506 | 1493 | a′ | C–N stretch |
| 1456 | 1473 | 1462 | — | a′ | C–N stretch |
| 1440 | — | — | — | a′ | ring stretch |
| 1422 | 1410 | 1425 | — | a′ | C–H in-plane bending |
| — | — | 1387 | 1400 | a′ | $NH_2$ rock |
| 1340 | 1339 | — | 1334 | a′ | ring stretch |
| — | — | 1276 | — | a′ | C–$NH_2$ stretch |
| — | — | 1245 | 1251 | a′ | $NH_2$ rock |
| 1230 | — | 1212 | 1215 | a′ | ring stretch |
| — | — | 1108 | — | a′ | $NH_2$ twisting |
| 1090 | — | 1077 | — | a′ | ring stretch |
| 1008 | — | 1016 | — | a′ | ring in-plane bending |
| — | — | 880 | — | a′ | C–N in-plane bending |
| 781 | 784 | — | — | a′ | C–Cl stretch |
| 742 | 734 | — | — | a′ | C=O in-plane bending |
| 680 | 668 | — | — | a′ | ring in-plane bending |
| — | 639 | — | — | a′ | C=O in-plane bending |
| 610 | 618 | — | — | a′ | C–Cl in-plane bending |
| 542 | 548 | 552 | — | a′ | ring in-plane bending |
| 946 | — | — | — | a″ | N–H out-of-plane bending |
| 865 | — | 863 | — | a″ | N–H out-of-plane bending |
| 815 | — | 805 | — | a″ | C–H out-of-plane bending |
| 756 | — | 767 | — | a″ | ring out-of-plane bending |
| — | — | 749 | — | a″ | $NH_2$ wagging |
| — | — | 488 | — | a″ | $NH_2$ torsion |
| 445 | — | 438 | — | a″ | C=O out-of-plane bending |
| 428 | — | — | — | a″ | ring out-of-plane bending |

**Table I.** (Contd.)

| 5-Chloro-uracil | | 5-Amino-uracil | | Symmetry species | Assignment |
|---|---|---|---|---|---|
| IR | Raman | IR | Raman | | |
| 412 | 420 | 418 | — | $a''$ | C=O out-of-plane bending |
| 234 | — | — | — | $a''$ | C N out-of-plane bending |
| — | 141 | — | 134 | | lattice |
| — | 125 | — | | | lattice |
| — | 101 | — | 100 | | lattice |
| — | 90 | — | — | | lattice |
| — | 78 | — | — | | lattice |

symmetric one. The $NH_2$ asymmetric stretch modes have been identified at 3370 and 3295 $cm^{-1}$ respectively in the IR spectrum of 5-aminouracil in conformation with the assignments proposed by Aruna and Shanmugam (1985) for 6-amino-2-thiouracil.

The neutral form of uracil and its substituted derivatives have three double bonds and their stretching vibration are expected to give rise to three strong infrared bands in the region 1500-1700 $cm^{-1}$. Out of the three, two strong bands at 1705 and 1677 $cm^{-1}$ in the IR spectrum of 5-chlorouracil and at 1740 and 1672 $cm^{-1}$ in the IR spectrum of 5-aminouracil are assigned to the two C=O stretching fundamentals. No such vibration was observed in the Raman spectrum of 5-aminouracil, whereas one of these modes could be observed at 1676 $cm^{-1}$ in the Raman spectrum of 5-chlorouracil. The third vibration at 1632 and 1625 $cm^{-1}$ in the IR and Raman spectra, respectively, of 5-chlorouracil and at 1615 and 1645 $cm^{-1}$ in the IR and Raman spectra respectively of 5-aminouracil have been associated with C=C stretching vibration. These assignments are in agreement with those available for uracil (Susi and Ard 1971), and mono and disubstituted uracil (Sanyal *et al* 1977). In the IR spectra of 5-chlorouracil, the 1677 $cm^{-1}$ band appears to be a closely spaced doublet. This splitting may be due to crystal field effect as suggested by Sanyal *et al* (1977). The space group of the 5-chlorouracil crystal is $P2_1/c$, with $a=8.450$, $b=6.886$, $c=11.419$ Å and $\beta=123.93°$.

The $NH_2$ group has scissoring, rocking, twisting and wagging modes of bending vibrations. The bands observed at 1588, 1387 and 1108 and 749 $cm^{-1}$ in IR spectrum of 5-aminouracil have been assigned as scissoring, rocking, twisting and wagging modes respectively. The band observed at 1400 $cm^{-1}$ in Raman spectrum of 5-aminouracil has been assigned to $NH_2$ rocking mode. These assignments find support from the works of Aruna and Shanmugam (1985).

The N–H in-plane bending vibrations have been identified at 1508 and 1417 $cm^{-1}$ in uracil (Shimanouchi *et al* 1964), at 1590, 1525 $cm^{-1}$ in 6-amino-

uracil and at 1550, 1510 $cm^{-1}$ in 6-amino-2-thiouracil (Aruna and Shanmugam 1985). In consonance with these assignments the bands observed at 1560, 1542 $cm^{-1}$ in the IR spectrum of 5-chlorouracil and at 1556, 1541 $cm^{-1}$ in the IR spectrum of 5-aminouracil have been identified as N–H in-plane bending vibration. The N–H out-of-plane bending vibrations have been identified at 865 and 946 $cm^{-1}$ in the IR spectrum of 5-chlorouracil and at 863 $cm^{-1}$ in the IR spectrum of 5-aminouracil.

The C=O in-plane bending vibration could only be observed in 5-chlorouracil at 742 $cm^{-1}$ in the IR spectrum and at 734 and 639 $cm^{-1}$ in the Raman spectrum. The C=O out-of-plane bending modes could be identified at 445 and 412 $cm^{-1}$ in the IR spectrum and at 420 $cm^{-1}$ in the Raman spectrum of 5-chlorouracil and at 438 and 418 $cm^{-1}$ in the IR spectrum of 5-aminouracil.

The ring out-of-plane bending modes have been observed at 756 and 428 $cm^{-1}$ in 5-chlorouracil and at 767 $cm^{-1}$ in 5-aminouracil.

Below 200 $cm^{-1}$ five lines in the Raman spectrum of 5-chlorouracil and two lines in the Raman spectrum of 5-aminouracil have been observed, which are in a region where lattice modes associated with C=O···H–N hydrogen bonds are expected.

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